

## Magnetic Susceptibility, Freezing Point Diagram, Density, and Spectral Absorption of the System Vanadium TetrachlorideCarbon Tetrachloride

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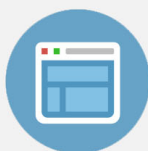
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# Magnetic Susceptibility, Freezing Point Diagram, Density, and Spectral Absorption of the System Vanadium Tetrachloride-Carbon Tetrachloride

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ON the basis of results of freezing point lowering experiments, it was reported by Simons and Powell<sup>1</sup> that an equilibrium existed between  $\text{VCl}_4$  and  $\text{V}_2\text{Cl}_8$  in carbon tetrachloride solution. Since vanadium tetrachloride is an odd molecule, it was implied that dimerization could take place, as in nitrogen dioxide, such that the odd electrons become paired. In the present paper are reported the results of a study on the system by means of magnetic susceptibility measurements, freezing point diagram determination, and spectral absorption of the solution, as a function of concentration of vanadium tetrachloride in carbon tetrachloride.

## PREPARATION OF THE MATERIALS

The vanadium tetrachloride was prepared by passing dry chlorine over about 3.4-inch mesh lumps of ferrovanadium in a 4- by 40-cm Pyrex tube at 400° to 450°C. The chlorine was dried by bubbling it through concentrated sulfuric acid; a sintered glass served as a gas disperser. The composition of the ferrovanadium used was: vanadium, 50 to 55 percent; silicon, 4.0 percent; carbon, 1.0 percent; iron, 45 to 50 percent. The large iron content caused the reaction tube to clog readily with the ferric chloride which condensed just outside the heated zone. To minimize the effect, a three-inch bulb was sealed onto the reaction tube at this location, the furnace lining was made of copper to give a more even distribution of heat to the reaction tube to the very end of the furnace, and a reaction temperature was maintained well above the sublimation temperature of ferric chloride.

The chief impurities in the crude product were silicon chlorides, which were easily removed by distillation at atmospheric pressure. It was

found that mixing the crude product with an equal volume of dry carbon tetrachloride helped to get rid of the silicon chlorides in the distillation process. The distillation column was 30 cm long, and was packed with glass spirals. When the carbon tetrachloride and silicon chlorides were distilled off and the temperature at the top of the column reached about 148°C, the system was then evacuated to about 30 mm Hg and samples of about 50 cc each were collected. Four large batches were made this way, and each time the analysis of the finished product was about the same: vanadium, 26.38 percent; chlorine, 73.13 percent—the theoretical values are 26.43 percent and 73.57 percent, respectively.

Vanadium was determined by dissolving the sample in water and fuming out the chloride ion with sulfuric acid. The resulting solution was then diluted, the vanadium was reduced with sodium bisulfite, excess  $\text{SO}_2$  boiled out, and the resulting vanadyl solution was titrated with standardized permanganate solution. Chlorine was determined by carefully placing a sample in water so that the hydrogen chloride formed in the vigorous reaction between vanadium tetrachloride and water could not escape. The chloride ion in the resulting solution was then determined as silver chloride by standard gravimetric methods.

## MAGNETIC STUDIES

### Apparatus

Magnetic measurements were made by the Gouy method.<sup>2-4</sup> The magnet was water cooled and run by large storage batteries. Currents between 10 and 15 amperes which gave fields in the range of 7200 to 8500 gauss were employed. Magnet currents could be held constant to

\* du Pont Fellow in chemistry at the California Institute of Technology.

\*\* Some of the material in this paper was presented by one of us (D.M.Y.) in the Julius Stieglitz Memorial lecture at the University of Chicago in April 1946.

<sup>1</sup> J. H. Simons and M. G. Powell, *J. Am. Chem. Soc.* **67**, 75 (1945).

<sup>2</sup> Pierce W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1943), p. 2.

<sup>3</sup> Wilhelm Klemm, *Magnetochemie* (Akademische Verlagsgesellschaft, Leipzig, 1936), p. 50.

<sup>4</sup> L. F. Bates, *Modern Magnetism* (Cambridge University Press, Nottingham, 1939), p. 97.

TABLE I. Susceptibilities and densities of solutions of vanadium tetrachloride in carbon tetrachloride (series 3 and 4 at 25.4°C).

Conc. VCl <sub>4</sub> (mole fract.)	Suscept. solution $\chi \times 10^6$	Suscept. mole VCl <sub>4</sub> $\chi_m \times 10^6$	$\mu_{\text{eff}}$ of VCl <sub>4</sub> *	Density of solution g/cc
1.000	6.031**	1163**	1.672**	1.8255**
0.7625	4.689	1149	1.662	1.7702
0.4983	3.104	1145	1.659	1.7078
0.2542	1.474	1142	1.657	1.6490
0.1331	0.5933	1137	1.654	1.6173
1.000	5.923	1142	1.657	1.8198
0.7615	4.653	1142	1.657	1.7695
0.4639	2.849	1136	1.653	1.6984
0.3188	1.896	1130	1.649	1.6632
0.1772	0.9043	1129	1.648	1.6278
0.0876	0.2379	1120	1.641	1.6056
0.0445	-0.0918	1106	1.631	1.5947

\*  $\mu_{\text{eff}}$  moment in effective Bohr magnetons.\*\* These may have contained some VCl<sub>3</sub>.

within 0.02 ampere for sufficient time to make a single measurement. The magnet pole pieces were eight centimeters in diameter at the base and tapered sharply to 4 cm at the faces. Pole faces were 2.5 cm apart. The balance used was capable of measuring weight changes to about 0.2 milligram.

The sample tube was the usual partitioned type with upper and lower sections, except that the upper section was fitted with a specific gravity bottle top plus a cap, so that density and magnetic measurements could be made at the same time. The volume of the upper section was determined with freshly distilled water and was found to be  $45.822 \pm 0.002$  cc at 25.3°C. Surrounding the sample tube region was an air thermostat equipped with heaters, fan, and a mercury thermoregulator. The temperature of the thermostat could be held constant to within  $\pm 0.1^\circ\text{C}$ .

### Calibration of Apparatus

A nickel chloride solution containing about 28 percent NiCl<sub>2</sub> by weight was used to calibrate the apparatus. The solution was prepared by dissolving "reagent grade"\*\*\* NiCl<sub>2</sub>·6H<sub>2</sub>O in distilled water. A gravimetric determination of nickel ion was made on the solution by means of dimethylglyoxime. The gram susceptibility of nickel chloride solution<sup>5</sup> was taken as  $\chi = [(10030X/T) - 0.720(1 - X)] \times 10^{-6}$ , where  $T$

\*\*\* Some reagent grade NiCl<sub>2</sub>·6H<sub>2</sub>O was found to contain intolerable amounts of manganese salts which were not mentioned in the analysis on the label.

<sup>5</sup> H. R. Nettleton and S. Sugden, Proc. Roy. Soc. A173, 313 (1939).

is the absolute temperature and  $X$  the weight fraction of NiCl<sub>2</sub> in solution.

It was found more convenient to evaluate an "apparatus constant" rather than attempt to measure absolute values of magnetic fields. This was done by measuring the pull at certain magnet currents on the sample tube to be used when the top half was filled with a nickel chloride solution of known susceptibility and the bottom half contained air at a pressure of one atmosphere. The "apparatus constant" is simply the change in pull divided by the difference between the susceptibility of the solution and air. This gives an apparatus constant corresponding to particular values of magnet current only. It automatically takes into account effects of residual fields, non-uniformity of the tube diameter, absolute field strengths, and the acceleration due to gravity, and lumps them into one constant that is easy to determine. The apparatus constant had to be checked before and after each series of determinations, since the magnet iron appeared to show slight changes with usage. Nickel chloride solutions also appeared to change slightly over a period of several months so that fresh solutions were used for each calibration. It was found that the pull on the tube was not affected by changing the position of the tube with respect to the magnetic field within easily reproducible limits. The empty sample tube showed a slight change in pull with

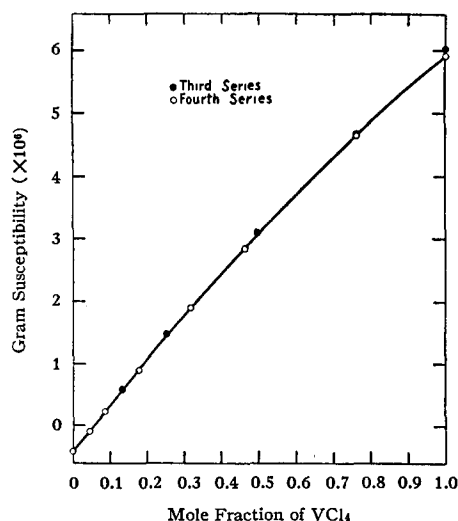


FIG. 1. Gram susceptibility for the system vanadium tetrachloride-carbon tetrachloride at 25.3°.

field, but the correction was small (0.0003 g) and affected measurements on dilute solutions only.

### Measurements

Magnetic and density measurements on pure vanadium tetrachloride and on the more concentrated solutions (50 percent or greater) were made as soon as possible after each preparation to avoid any errors that might arise due to decomposition; the more dilute solutions were fairly stable. The carbon tetrachloride used was dried for at least one week over anhydrous magnesium perchlorate. Table I shows the results obtained. The values of  $\mu_{\text{eff}}$  were calculated according to the relation  $\mu_{\text{eff}} = 2.83(\chi_m T)^{1/2}$ , where  $\chi_m$  is the experimental value given in column three, Table I, and  $T$  is the absolute temperature.

Four such series were run, but the first two were not acceptable as quantitatively correct. However, the first two series showed the same general behavior as the last two, and it is believed that the small variation of mole susceptibility with concentration is a real effect even though accurate values are not easy to get as the solutions become more dilute. The susceptibility of the solutions was not precisely a linear function of the concentration, as may be seen in Fig. 1. Each susceptibility value is the average of three (for series 3) or four (series 4) measurements on the same solution at different field strengths; such experiments showed the susceptibility of the solutions to be independent of the field strengths employed. The mass susceptibility and density of the carbon tetrachloride used were found to be  $-0.432 \times 10^{-6}$

TABLE II. Effect of temperature on the magnetic susceptibility of vanadium tetrachloride.

Abs. temp.	$\chi_m (\times 10^6)$	$\chi_m T$	$\theta$
274 $\pm 1$	1234	0.365	-7
298.9 $\pm 0.2$	1152	0.373	1
328.7 $\pm 0.7$	1041	0.375	2

and 1.5837 g/cc at 25.3°C, respectively. The corresponding values from the *International Critical Tables*<sup>6</sup> are  $-0.429 \times 10^{-6}$  and 1.58376 g/cc at 25.3°C.

The values in Table I were calculated in the following manner:

$$\chi = (1/\rho)[(\Delta W/C) + K_a]$$

and

$$\chi_m = 192.78[(1/\rho f)[(\Delta W/C) + K_a] + 0.432[(1-f)/f] \times 10^{-6}],$$

where  $\rho$  is the density of the solution,  $f$  is the weight fraction of vanadium tetrachloride in the solution,  $\Delta W$  is the change in pull in grams on the sample from zero magnet current to full current,  $K_a$  is the volume susceptibility of air, which was taken as  $0.027 \times 10^{-6}$  for the general laboratory conditions of 25° and 750 mm Hg, and  $C$  is the apparatus constant calculated as previously described.

The magnitude of  $\Delta W$  ranged from 0.7387 gram for pure  $\text{VCl}_4$  to  $-0.0124$  gram for the most dilute solution at maximum field strength. Apparatus constants ran something as follows: at a magnet current of 10 amperes  $C = 5.003 \times 10^4$ , at 15 amperes  $C = 6.878 \times 10^4$ , for the fourth series.

The specific volume of the system (Fig. 2) shows that the volume of the solution is generally slightly less than the sum of the volumes of the pure components. The observed density of pure vanadium tetrachloride was 1.8198 g/cc at 25.3°C and agrees fairly well with the interpolated value of 1.8187 g/cc at 25.3°C from the data given by Roscoe.<sup>7</sup>

### Variation of Susceptibility with Temperature

Magnetic susceptibility measurements were made on a fresh sample of vanadium tetra-

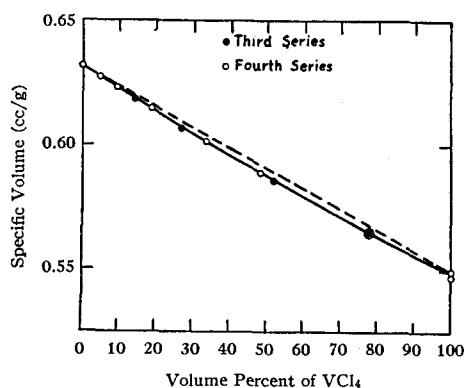


Fig. 2. Specific volume for the system vanadium tetrachloride-carbon tetrachloride at 25.3°.

<sup>6</sup> *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1930), Vol. 6, p. 361; Vol. 3, p. 28.

<sup>7</sup> K. S. Gibson and M. M. Balcom, *J. Opt. Soc. Am.* **37**, 593 (1947).

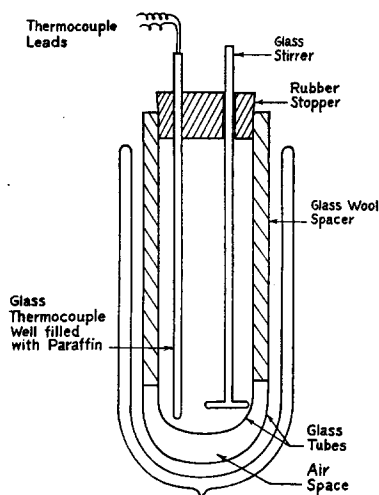


FIG. 3. Freezing point apparatus.

chloride at three different temperatures. Since the apparatus was not well adapted for this type of work, the temperature range was rather narrow. The results are given in Table II. In calculating the values of  $\chi_m T$  a diamagnetic correction of  $-98 \times 10^{-6}$  was used. The  $\theta$  values were calculated from the Curie-Weiss formula  $\chi_m [C/(T-\theta)]$ , using 0.372 (assuming the theoretical value for one unpaired electron) as the value of the Curie constant. Experimental errors plus the uncertainty in the diamagnetic correction cause an uncertainty in  $\theta$  of a magnitude about equal to the average value of  $\theta$ .

#### FREEZING POINT DIAGRAM

The freezing point diagram of the system, vanadium tetrachloride-carbon tetrachloride, was determined by running cooling and warming curves on solutions of known composition. A diagram of the apparatus used is shown in Fig. 3. Carbon tetrachloride and mercury freezing points were used to determine an apparatus correction. The thermocouple was a calibrated copper constantan couple with the cold junction in crushed clean ice in a small amount of distilled water. A Leeds and Northrup Type K potentiometer and type HS galvanometer arrangement was used to measure to e.m.f. of the couple. The sample was stirred continuously. Each sample was analyzed before and after the cooling and warming curves were taken.

Samples containing 70 percent vanadium tetra-

chloride by weight or less showed changes in composition of about 0.4 percent during the course of an experiment which lasted about five hours. The 80 percent sample decreased in concentration by about 1.5 percent during a run. All samples showed marked supercooling. In all cases the breaks in the cooling curves occurred at a lower temperature than the corresponding breaks in the warming curves. Each point reported is an arithmetic average of two such temperatures. Figure 4 shows the results obtained. The accuracy claimed for each temperature is not greater than  $\pm 1^\circ\text{C}$ , except for the eutectic, which is good to about  $\pm 0.5^\circ\text{C}$ . The eutectic temperature was  $-64.0^\circ\text{C}$ ; the freezing point of pure vanadium tetrachloride was  $-25.7^\circ\text{C}$ . This latter temperature agrees well with the value  $-25.7^\circ\text{C}$  given by Simons and Powell.<sup>1</sup> The eutectic composition occurs at 0.37 mole fraction, and the solidus lines reach the eutectic temperature at 0.17 and 0.62 mole fraction of vanadium tetrachloride. It was quite difficult to obtain cooling or warming curve breaks corresponding to points on the liquidus curve in the concentration range about 0.23 mole fraction.

#### LIGHT ABSORPTION STUDIES

Light absorption data were obtained by means of a Beckman spectrophotometer. Measurements were made over the wave-length range from 4000Å to 12,000Å, although it was realized that readings beyond about 10,000Å are of ques-

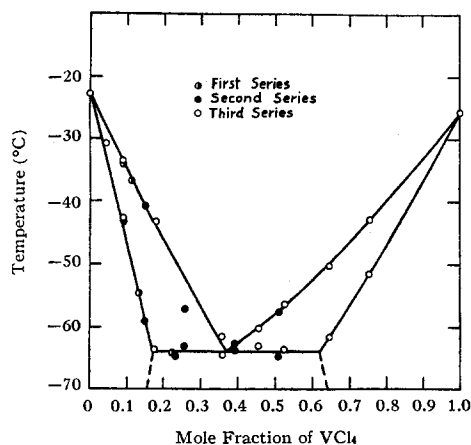


FIG. 4. Freezing point diagram for the system vanadium tetrachloride-carbon tetrachloride.

tionable value.<sup>7</sup> Corex cells were used, and the path length was one centimeter. The cells were sealed shut immediately after filling to avoid introduction of moisture. This was particularly important for the dilute solutions, since a small amount of moisture could change the concentration in the cell considerably from that of the part of the solution actually analyzed. Because of this effect, reliable results could not be obtained on solutions of concentrations less than about 0.01 mole per liter of solution. Some of the absorption curves are shown in Fig. 5. The behavior of these solutions with respect to Beer's law was investigated in various regions of the spectrum. Some such curves are shown in Fig. 6. The character of these curves suggested that a polymerization reaction might be involved. To investigate this, the apparent molal absorption coefficient was calculated at various wave-lengths according to the formula

$$\log_{10}(I_0/I) = (l/2.3)b_m c,$$

where  $\log_{10}(I_0/I)$  is the extinction coefficient,  $b_m$  the apparent molal absorption coefficient,  $l$  the path length of the light in cm, and  $c$  is the concentration of solution in moles/liter of solution. Some of the results are shown in Table III.

The data in Table III seem to indicate that the absorption in the region between 9000Å and 12,000Å may be due largely to a monomer, and the strong absorption starting about 7000Å and extending to shorter wave-lengths may be due to one or more polymers. Although the values of  $b_m$  in the monomer region increase as the concentration decreases, they do not approach a limit at zero concentration in the manner one would ordinarily expect. Indeed, as far as the values are concerned it can be shown empirically that  $1/b_m$  appears to be a linear function of the concentration for the more dilute solutions. It may happen, however, that limiting value of  $b_m$  will be reached rather suddenly in the concentration range between  $6.4 \times 10^{-3}$  and zero moles per liter.

#### HEAT OF SOLUTION

As a side experiment in the course of this work, a single semi-quantitative experiment was performed on the heat of dilution of vanadium tetrachloride by carbon tetrachloride. About 1.4

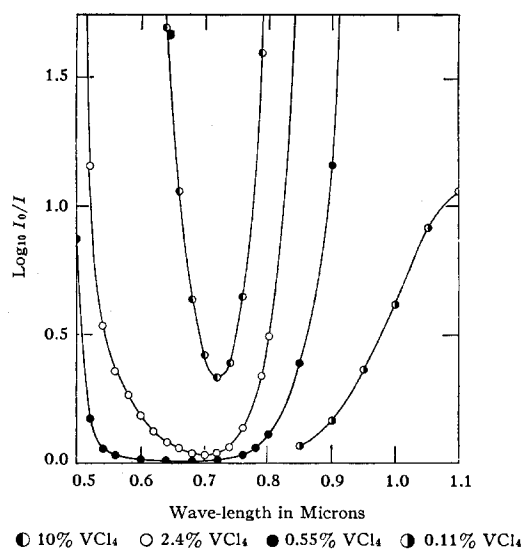


FIG. 5. Absorption spectrum of solutions of vanadium tetrachloride in carbon tetrachloride.

moles of vanadium tetrachloride were diluted with about 1 mole of carbon tetrachloride; a thermometer immersed in the solution showed a temperature drop of 7°C. This corresponds to the absorption of about 420 calories per mole of vanadium tetrachloride when diluted to about 63 percent by weight.

It is interesting to note that this system is anomalous in that the density data indicate a negative deviation from Raoult's law, but the heat of dilution result points to a positive deviation. This situation is not without precedence, however.<sup>8</sup>

#### DISCUSSION

Vanadium tetrachloride is a molecule having one odd electron per vanadium atom; hence, on the basis of the formula derived from quantum statistics for non-interacting magnetic dipoles, the paramagnetic susceptibility per mole of this compound could be expected to be  $1247 \times 10^{-6}$  c.g.s. unit at 25.3°C. A diamagnetic correction can be estimated by taking  $\chi_m'$  for each chlorine<sup>9</sup> as  $-22 \times 10^{-6}$  and for vanadium<sup>10</sup>  $\chi_m'$  as  $-10 \times 10^{-6}$ ; this gives a diamagnetic susceptibility for the whole molecule of  $-98 \times 10^{-6}$  c.g.s. unit per mole. Hence, the predicted susceptibility of

<sup>8</sup> J. H. Hildebrand, *Solubility* (The Chemical Catalog Company, Inc., New York, 1924), p. 63.

<sup>9</sup> K. Ikenmeyer, *Ann. Phys.* (5) **1**, 169 (1929).

<sup>10</sup> W. R. Angus, *Proc. Roy. Soc.* **136A**, 569 (1932).

TABLE III. Apparent molal absorption coefficients of solutions of VCl<sub>4</sub> in CCl<sub>4</sub>.

Conc. in moles/l of sol.	Wave-length A						
	12000	11000	10000	9000	8000	7000	6000
$6.41 \times 10^{-3}$	262.0	308	181	45.2	8.6		
$9.05 \times 10^{-3}$	232.0	267	160	42.7	(10.4)		
$2.63 \times 10^{-2}$	142.0	252	209*	63.0*	(7.5)		
$4.52 \times 10^{-2}$	86.4		153	59.2	5.5	0.3	0.8
$6.16 \times 10^{-2}$	69.0		105	63.8	6.2	1.0*	1.8*
$9.06 \times 10^{-2}$	48.8				5.6	0.4	1.2
$1.98 \times 10^{-1}$	25.1				5.8	0.4	2.2
$4.81 \times 10^{-1}$					5.6	6.6	5.2
$9.19 \times 10^{-1}$					5.6	10.7	8.5

\* Readings on the Beckman were always started in the long wave-length region, and it usually happened that solutions went bad before all readings could be taken. It required about an hour to take a complete set of readings.

vanadium tetrachloride is approximately  $1149 \times 10^{-6}$  c.g.s. unit per mole, which is in good agreement with the average experimental value of  $1152 \times 10^{-6}$  c.g.s. unit per mole. From this one may infer that the vanadium tetrachloride molecules act as essentially independent, non-interacting magnetic dipoles, or, at least if a polymer is formed, there is no coupling of the odd electrons as occurs in, say, nitrogen dioxide. Also, the change in mole susceptibility with concentration of vanadium tetrachloride in carbon tetrachloride solution (Fig. 7) shows a small decrease with a decrease in concentration, which is exactly opposite to what would be expected if the odd electron were involved in a polymerization reaction.

Actually, if no reactions or interactions be-

tween molecules take place, the mole susceptibility of vanadium tetrachloride should be independent of concentration. However, in paramagnetic solutions this case is rarely observed over a wide range of concentrations. It is interesting to note that solutions of ferric chloride<sup>11</sup> in water behave in very much the same way as the solutions studied here. However, in the water system the decrease in susceptibility is attributed mainly to the hydrolysis of the ferric ion. In the case at hand, reaction with carbon tetrachloride does not seem very likely.

The freezing point diagram in Fig. 4 shows clear evidence of the existence of limited solid solution formation in this system. In the treatment of their freezing point lowering data, Simons and Powell<sup>1</sup> assumed pure carbon tetrachloride to be solid phase. It is now clear that conclusions based on such a treatment are not valid. The experimental results of Simons and Powell are in agreement with the phase diagram in Fig. 4 in that their freezing points fall very close to the liquidus curve, and that the freezing point lowering is not as great when the observed solid solutions form as when pure solvent crystallizes out. Hence, the data would have the same general character if a polymerization were involved and pure solvent did crystallize out, as it has when solid solution crystallizes out.

The heat of fusion of vanadium tetrachloride can be calculated approximately from the phase diagram by the use of the equation<sup>12</sup>

$$\Delta H_1/RT^2 = -(dN_2/dT) - (dN'_2/dT),$$

in which  $R$  is the gas constant,  $T$  the melting point of solvent,  $\Delta H_1$  the heat of fusion of solvent,  $(dN_2/dT)$  the limiting rate of change of solute in liquid solution with temperature, and  $(dN'_2/dT)$  the limiting rate of change of solute in solid solution with temperature. The heat of fusion of vanadium tetrachloride turns out to be about 550 cal./mole. The entropy of fusion is then about 2.2 entropy units per mole which is about right for a normal liquid.

The phase diagram is probably in error because the cooling and warming curves were de-

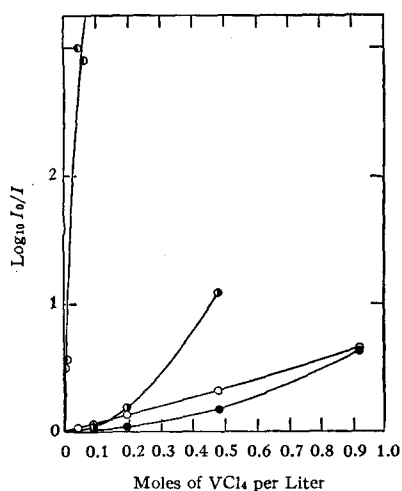


FIG. 6. Beer's law plot for Fig. 5.

<sup>11</sup> E. C. Stoner, *Magnetism and Matter* (Methuen and Company, Ltd., London, 1934), p. 326.

<sup>12</sup> G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), p. 238.

terminated over a rather short period, and the solid was annealed for only about 20 minutes. As a result, it can be argued that the region between the liquidus and solidus curves should be narrower than shown. The points on the liquidus curve are probably all right, but the points on the solidus curve may be too far over toward the corresponding pure components. This can come about because the solid solutions are richer in solvent than the corresponding liquid solutions; hence, if the solid solutions do not dissolve and reform as the temperature decreases, the final solution that freezes will correspond to a composition closer to the eutectic than the original composition. This means that all the points should be shifted toward the eutectic composition, which causes a narrowing of the regions between the liquidus and solidus curves. As a result, the phase diagram should give entropy of fusion values that are too large. However, the entropy of fusion of carbon tetrachloride given by Fig. 4 turns out to be 2.1 e.u., but the literature value is 2.56 e.u. Hence, it is more likely that the entropy of fusion found for vanadium tetrachloride is low rather than high, and that other effects were operative which overbalance the effect discussed above.

In order to analyze the light absorption data in a conventional way, it is necessary to find  $b_m^0$  monomer. This is obtained by extrapolating the apparent  $b_m$  to zero concentration taken at a wave-length at which the principal absorber is monomer. As was pointed out earlier, this is not easy to do in the case at hand. However, reasonable values of  $b_m^0$  monomer can be estimated without causing serious difficulties in discussing the data. The absorption values taken at 10000Å and 11000Å will be taken for discussion. Reasonable extrapolated values of  $b_m^0$  monomer at these wave-lengths are 182 and 312, respectively. Now, the concentration of monomer at any total concentration can be obtained from  $C_1 = C_m^b / b_m^0$ , where  $C_1$  is the concentration of monomer,  $C$  the total concentration from analysis,  $b_m$  the apparent molal absorption coefficient, and  $b_m^0$  the molal absorption coefficient of monomer, provided values of the  $b$ 's are taken in regions where only monomer absorbs light. For simplicity the polymerization reaction  $nA \rightleftharpoons A_n$  was assumed. If this reaction occurs,

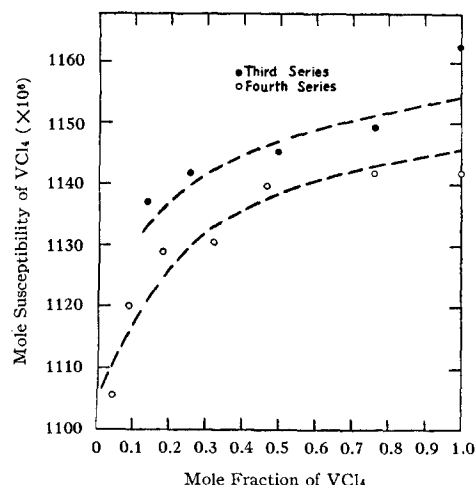


FIG. 7. Mole susceptibility of vanadium tetrachloride in carbon tetrachloride solutions at 25.3°.

then it can be shown that

$$\log(C - C_1) = n \log C_1 + \log C_n K,$$

$$C = C_1 + nC_n; \quad K = (C_n / C_1^n),$$

where  $C_n$  is the concentration of polymer and  $K$  the equilibrium constant for the assumed reaction. In Fig. 8 there is shown a plot of  $\log(C - C_1)$  versus  $\log C_1$ . The points appear to follow roughly a linear relation, considering all the approxima-

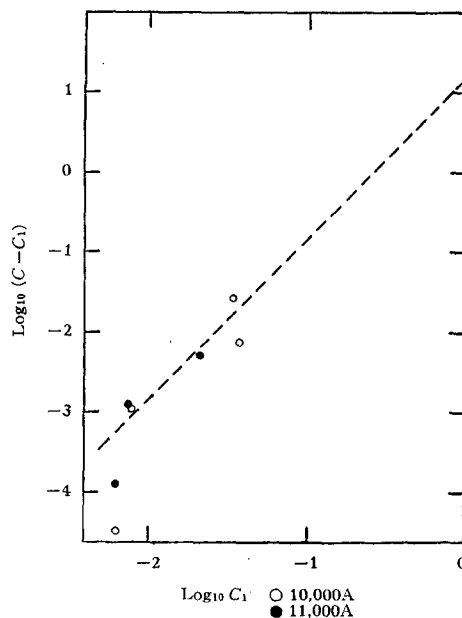


FIG. 8. Relation between the logarithm of the concentration of polymer, and the logarithm of the concentration of monomer at about 25°.



TABLE IV. Variation of the mole absorption coefficient of "dimer" with total concentration.

Total conc. formality ( $\times 10^3$ )	Conc. of "monomer" ( $\times 10^3$ )	Conc. of "dimer" ( $\times 10^3$ )	Log $I_0/I$ at 6000Å	$b_d^0$
4.52	3.07	0.73	0.0157	4.95
9.06	5.12	1.97	0.0473	5.52
19.8	8.60	5.60	0.189	7.76
48.1	14.8	16.7	1.09	15.0
91.9	21.5	35.2	3.40	22.2

tions made and the inaccuracies involved in measuring the low concentrations. The dashed straight line has a slope of two and  $K=7.6$ . However, this relation does not hold as the solutions become more concentrated. This is shown by the data in Table IV. The value of  $b_d^0$ , the absorption coefficient of "dimer," was calculated assuming the values of  $n$  and  $K$  given above. It is clear that  $b_d^0$  is not constant, but increases with increasing concentration. Unfortunately, not enough data was obtained to identify clearly the source of the observed deviations from Beer's law.

An experimental value for the diamagnetism of vanadium tetrachloride is not available, but values calculated by the method of Angus<sup>11</sup> seem to be rather reliable and the value  $-98 \times 10^{-6}$  is probably not in error by more than four or five percent. This makes the measured susceptibility of pure vanadium tetrachloride agree, within experimental error, with the calculated susceptibility of noninteracting magnetic dipoles. Van Vleck<sup>13</sup> has shown that polyatomic molecules should have a paramagnetic susceptibility somewhat greater than this by a term which he calls the high frequency constant paramagnetism, but it may be that the vanadium tetrachloride molecule is sufficiently symmetrical to make this term negligible.<sup>14</sup> This situation makes it difficult to explain the variation of

susceptibility with concentration. It may be that the peculiar effects encountered in solids are beginning to show up. The fact that  $\theta$  appears to be a function of the temperature is some indication that something out of the ordinary is involved.

Unfortunately, there are not enough experimental data to make it possible to give a definite explanation of the observed variation of susceptibility. The theoretical value of Curie's constant for  $J=\frac{1}{2}$  was assumed in order to calculate  $\theta$ . Actually, the value of Curie's constant may differ from the theoretical value for pure vanadium tetrachloride and it may be a function of concentration. It would be interesting to measure susceptibilities of pure vanadium tetrachloride and its solutions in carbon tetrachloride over a sufficient temperature range to determine Curie's constant and  $\theta$  experimentally with reasonable accuracy. In addition, it would be well to know the susceptibility of vanadium tetrachloride in the vapor phase so as to have a value essentially free from possible effects of the interactions between molecules.

Because the thermodynamic properties of vanadium tetrachloride indicate that the liquid is normal, it is not likely that definite polymers are actually formed in the liquid phase. It may be that both the departure from Beer's law and the variation of susceptibilities with concentration result from the same basic cause. However, the light absorption and the magnetic studies would have to be greatly extended in order to establish this.

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<sup>13</sup> J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932), p. 195.

<sup>14</sup> Reference 13, p. 277.